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<p>(21) International Application Number: PCT/US98/03270</p> <p>(22) International Filing Date: 3 March 1998 (03.03.98)</p> <p>(30) Priority Data:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 40%;">08/812,151</td> <td style="width: 40%;">6 March 1997 (06.03.97)</td> <td style="width: 20%; text-align: right;">US</td> </tr> <tr> <td>08/812,172</td> <td>6 March 1997 (06.03.97)</td> <td style="text-align: right;">US</td> </tr> <tr> <td>08/812,832</td> <td>6 March 1997 (06.03.97)</td> <td style="text-align: right;">US</td> </tr> <tr> <td>Not furnished</td> <td>27 February 1998 (27.02.98)</td> <td style="text-align: right;">US</td> </tr> </table> <p>(71) Applicants: SARNOFF CORPORATION [US/US]; CN 5300, Princeton, NJ 08543-5300 (US). SHARP CORPORATION, K.K. [JP/JP]; 22-22, Nagaïke-cho, Abeno-ku, Osaka 545 (JP).</p> <p>(72) Inventors: TORMEY, Ellen, Schwartz; 8 Jeffrey Lane, Princeton Junction, NJ 08550 (US). PRABHU, Ashok, Narayan; 21 Meadow Lane, East Windsor, NJ 08520 (US). SREERAM, Attigana, Narayanaswamy; 39-02 Fox Run Drive, Plainsboro, NJ 08536 (US). LIBERATORE, Michael, James; 208B Bakers Basin Road, Lawrenceville, NJ 08648 (US). PALANISAMY, Ponnusamy; 133 Claremont Drive, Lansdale, PA 19446 (US).</p> <p>(74) Agent: O'ROURKE, John, F.; Sarnoff Corporation, Patent Operations, CN 5300, Princeton, NJ 08543-5300 (US).</p>		08/812,151	6 March 1997 (06.03.97)	US	08/812,172	6 March 1997 (06.03.97)	US	08/812,832	6 March 1997 (06.03.97)	US	Not furnished	27 February 1998 (27.02.98)	US	<p>(81) Designated States: JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: CERAMIC MULTILAYER PRINTED CIRCUIT BOARDS WITH EMBEDDED PASSIVE COMPONENTS</p>														
<p>(57) Abstract</p> <p>Passive components such as capacitors, resistors, and RF filters can be made by screen printing suitable inks onto green tapes, completed with conductive layers (14, 15) below and above the component ink layers. The resultant green tape stack is then fired to form embedded capacitors. By laminating the green tape stack onto metal support board substrate, shrinkage in the x and y dimensions is limited and the components can maintain close tolerances. When many green tape layers are to be stacked, improved shrinkage is obtained when green tapes having a moderate amount of oxide fillers, e.g., less than about 15 % by weight of the green tape composition, are interleaved with green tape having higher amounts, e.g., above 25 % by weight, of oxide fillers.</p>														

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CERAMIC MULTILAYER PRINTED CIRCUIT BOARDS
WITH EMBEDDED PASSIVE COMPONENTS

This invention relates to multilayer, ceramic,
supported printed circuit boards that have low shrinkage in
two dimensions on firing. More particularly this invention
relates to metal supported, multilayer, ceramic printed
5 circuit boards that incorporate co-fired passive components.

BACKGROUND OF THE INVENTION

Ceramic compositions of crystallizing glasses are known
which, when mixed with non-crystallizing glasses, form green
tape compositions which can be adhered to metal core support
10 substrates, such as copper/nickel clad or plated kovar
plates. Kovar is a Fe/Co/Ni alloy commercially available
from Carpenter Technology. One such alloy includes 53.8
weight percent of iron, 29 weight percent of nickel, 17
weight percent of cobalt and 0.2 weight percent of
15 manganese. These alloys display a sharp change in their
coefficient of expansion at certain temperatures. They are
available with a 1 mil thick coating of copper and a 1 mil
thick coating of nickel on both sides of the kovar core.
They have a thermal coefficient of expansion (TCE) of 5.8
20 ppm/°C (RT to 300°C) and a thermal conductivity (z or
thickness direction) of 21.8 Watt/m°K.

To use these kovar plates as support substrates for
printed circuit boards, they are heat treated in air to
oxidize the nickel coating and then glazed with a bonding
25 glass, generally a $\text{CaO-Al}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3$ glass. The bonding
glasses can be screen printed onto the support substrate by
making a printable ink of the bonding glass powder mixed

with an organic binder and a solvent. The bonding glass is generally applied to a thickness of 40-70 microns on the support substrate. The bonding glass is then dried and densified by heating at 700-800°C. To improve the adhesion of the bonding glass to a kovar support, about 6% by weight of copper powder can be added to the bonding glass. These kovar support substrates prepared as above are used herein and, when co-laminated to low firing temperature green tape compositions, they prevent shrinkage of the ceramic layers in the x and y dimensions during firing.

Low firing temperature green tapes adhered to a metal core support board having a bonding glass thereon as described above are made from a mixture of crystallizing and non-crystallizing glasses.

Suitable crystallizing glasses for example contain 20-55% by weight of ZnO; 20-28% by weight of MgO; 10-35% by weight of B₂O₃; and 10-40% by weight of SiO₂. These glasses have a TCE matched to kovar, and they have low dielectric loss properties; however, they have a low crystallization temperature which inhibits densification of the glass on firing. Thus these glasses can be mixed with a lead-based, non-crystallizing glass. Suitably, these non-crystallizing glasses contain from 30-80% by weight of PbO; 15-50% by weight of SiO₂; up to 10% by weight of Al₂O₃; up to 15% by weight of B₂O₃; and up to 10% by weight of ZnO.

However, when the crystallizing glasses are mixed with lead-based, non-crystallizing glasses, the TCE is lowered and the dielectric loss properties are increased. The

lateral shrinkage (x and y) is still higher than desirable as well. The addition of minor amounts of oxide fillers, such as quartz, alumina, forsterite and the like, reduces the lateral shrinkage on firing, and thus these filler-
5 modified ceramics have desirable dielectric properties, low shrinkage during firing and a TCE matched to kovar.

Green tape compositions useful herein are formed by mixing suitable glass powders, including crystallizing glasses, generally of the $\text{ZnO-MgO-B}_2\text{O}_3\text{-SiO}_2$ type, with non-
10 crystallizing glasses and oxide fillers with an organic vehicle, generally including resin, solvent, dispersants and the like, and casting the resultant slurry into a thin tape, known as green tape.

Conductive inks can be screen printed onto the green
15 tapes to form circuit patterns. Several of the green tapes can be aligned and stacked and laminated under pressure. Via holes punched in the green tapes and filled with conductive inks, e.g., mixtures of a conductive metal powder, an organic vehicle and a glass, generally the same glass as
20 that used to make the green tape, provide a conductive path between the circuit patterns on different green tape layers. These laminated green tape stacks are then aligned with a support substrate coated with a bonding glass, and co-laminated, also under pressure. Since shrinkage occurs
25 mainly in the thickness (z) dimension during firing, the circuitry is not disturbed during firing and close tolerances can be maintained. These ceramics are compatible with low melt temperature conductive inks, such as silver-

based inks, used to form the electrically connected circuits on the various layers and to form bond pads and the like. Thus the ceramic circuit boards as described hereinabove have low dielectric loss properties and are useful for use with microwave/digital packaging.

Up to the present time, when multilayer ceramic circuit boards are to include passive components, such as resistors or capacitors, discrete components have been mounted to the top of the fired boards, using solder or epoxy type adhesives, to adhere the components to the multilayer ceramic. The addition of these components increases the number of steps needed to make these circuit boards, i.e., the components must be aligned and adhered to the ceramic multilayer board, and connected to a source of power. Further, in order to accommodate a number of discrete devices, the multilayer boards have to be large. Thus the costs of making such boards is high.

It would be advantageous to be able to screen print passive components onto particular green tapes of multilayer, low temperature co-fired ceramic circuit boards because the packing density can be increased, reducing the size and cost of the packaging, and the number of processing steps required can be reduced. Using the recently developed low firing temperature glasses and a metal support board that reduce shrinkage in the x and y dimensions, screen printing of such components to tight tolerances, and high precision placement, become feasible. Further, because fewer interconnects need to be made, reliability would also be

improved.

However, it is difficult to maintain reduced shrinkage during firing and to prevent de-lamination of the green tape stacks from the support substrate when a plurality of green
5 tapes are aligned and fired with components therebetween.

SUMMARY OF THE INVENTION

We have found that passive components, such as capacitors, resistors and RF components, can be embedded in green tape stacks made of suitable glasses on a support
10 substrate that prevents shrinkage in the x and y dimensions. Suitable capacitor or resistor inks and conductive layers can be screen printed onto green tapes, embedded between other green tapes, laminated and fired at fairly low temperatures, i.e., 850-900°C, without de-laminating from the
15 support and without shrinkage in the x and y dimensions so as to produce printed circuit boards with close tolerances that have embedded components therein.

Capacitor inks can be made from barium titanate, titanium oxide and lead magnesium niobate dielectrics,
20 which, when combined with appropriate glasses, sinter at low temperatures. The capacitor inks can be screen printed onto ceramic green tapes and connected to a silver conductor layer by means of vias in the green tape that are filled with appropriate conductive inks. After printing the passive
25 component precursor inks and other circuitry on the green tapes, multiple green tapes are aligned, laminated together and co-fired in air at a temperature of about 850-900°C. Capacitors can be made in a wide range of dielectric

constants.

Shunt capacitors can also be made by using a ground plane metal as the bottom capacitor plate. The capacitors are located one or more layers from the top of the stack.

5 Capacitors can be terminated by screen printing a conductive layer over and under the printed capacitor dielectric ink.

Thick film resistor inks can be made based on ruthenium oxide (RuO_2) and appropriate glasses that sinter at low temperatures, together with suitable organic vehicles. The
10 resistor inks are screen printed onto green tapes that are aligned and stacked on a support, and fired to produce embedded resistors having a wide range of resistor values and thermal coefficient of resistance (TCR) values. To adjust the TCR values, a small amount of barium titanate can
15 be added. The resistors are connected to a source of power with a conductive layer screen printed on top of the green tape stack. After printing the resistors and other circuitry, the multiple green tape layers are aligned, laminated together, applied to a metal support substrate via
20 a bonding glass, and co-fired in air at temperatures of from about 780-900°C to form printed circuit boards having embedded resistors therein that are stable and reliable.

When many green tape layers are to be stacked to produce a fired stack about 2 mm in thickness or higher, we
25 have found that de-lamination and shrinkage problems still occur. Thus we have further found that by interleaving green tape layers including low dielectric loss glasses that are mixed with minor amounts of oxide fillers with green tape

layers from the same glasses but now including greater amounts of oxide fillers, many more layers of green tapes can be stacked, laminated and fired with no shrinkage in the x and y directions, and with no de-lamination from a metal support substrate. These thick multilayer metal supported circuit board stacks are particularly useful when RF components are to be embedded in the stacks.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph of dielectric constant versus capacitor size for low dielectric constant inks.

Fig. 2 is a cross sectional view of one embodiment of a buried capacitor of the invention.

Fig. 3 is a graph of dielectric constant versus capacitor size for capacitors of the invention.

Fig. 4 is a graph of temperature coefficient of capacitance versus capacitor size for capacitors of the invention.

Fig. 5 is a graph of dielectric constant versus capacitor size for capacitors of the invention.

Fig. 6 is a graph of resistor area versus resistance and TCR for resistors having a first size.

Fig. 7 is a graph of resistor area versus resistance and TCR for resistors having a second size.

Fig. 8 is a cross sectional view of a multilayer ceramic circuit board of the invention having buried silver layers.

Fig. 9 is a cross sectional view of a multilayer ceramic circuit board of the invention having RF filters

embedded in the layers.

DETAILED DESCRIPTION OF THE INVENTION

The formulation of various capacitor inks, methods of formation and test results of embedded capacitors having differing dielectric constant and TCC will be discussed first.

We have discovered low dielectric constant, i.e., $K =$ about 50, capacitor inks based on barium titanate and titanium oxide powders. These powders sinter at high temperatures, about 1100-1300°C, and thus they must be modified by combining them with low melting glasses so that the barium titanate/glass or titanium oxide/glass compositions will sinter at lower temperatures of about 850-900°C, and to adjust the dielectric constant (K) and to minimize the temperature coefficient of capacitance (TCC).

Barium titanate is commercially available from the Degussa Company under the trade name AD302L, (designated below as D) and a mixture of barium titanate and barium tin oxide from the Ferro Corporation under the trade name YL12000 (designated below as F). The properties of these powders are set forth below in Table I, wherein K is the dielectric constant, the dielectric loss is $\tan\delta$ and the temperature is in degrees Centigrade. Particle size is given as average particle size in microns (μm).

TABLE I

	<u>Compo-</u> <u>sition</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC, %</u>	<u>Firing</u> <u>T, °C</u>	<u>Av. Part.</u> <u>Size, μm</u>
5	F	12000	0.022	-80*	1200	1.0
	D	3200	<0.02	- 9**	1140	0.6

10 * RT to 125°C

** 85°C

A suitable titanium oxide, #4162-01, is available from
Mallincrodt Baker Co.

Prior to making capacitor ink compositions, the barium
15 titanate or titanium oxide powder was mixed with various low
firing temperature glasses. The compositions of suitable
glasses, in weight percent, is given below in Table II.

TABLE II

	<u>Oxide</u>	<u>Glass 1</u>	<u>Glass 2</u>	<u>Glass 3</u>	<u>Glass 4*</u>	<u>Glass 5</u>	<u>Glass 6</u>
20	Al ₂ O ₃	6.00	10.10			1.0	1.82
	BaO				<2.0		
	B ₂ O ₃	39.00		19.60	>5.0	5.0	8.18
	Bi ₂ O ₃					23.0	
25	CaO	5.0					
	CdO					36.0	
	MgO			24.50			
	PbO		50.00		>70.0	25.0	68.82
	SiO ₂		39.90	24.50	< 2.0	5.0	2.23
30	TiO ₂						9.09
	ZnO	50.00		29.40	>12.0	5.0	9.09
	ZrO ₂						2.73
35	Particle 11- Size, μm 13		5-7	10-12	5.0	5.0	4.0

* Commercially available glass as SCC-11 from Sem Com, Inc.,
Toledo, OH

40 Representative low dielectric constant capacitor inks
were made from barium titanate powder admixed with various
glasses and glass mixtures, together with conventional
dispersants, resin and solvent, and screen printed onto

green tapes. The ink compositions are summarized in Table III below wherein the glass compositions are as shown in Table II.

TABLE III

	<u>BaTiO₃</u> <u>Type</u>	<u>Wt %</u>	<u>Glass#</u>	<u>Wt %</u>	<u>Dispersant</u>	<u>Resin</u>	<u>Solvent</u>
					<u>Wt %</u>	<u>Wt%</u>	<u>Wt %</u>
5	F	62.29	1	7.14	1.43	4.07	23.07
	F	66.09	1	8.25	1.52	4.84	19.38
10	F	64.89	2	9.8	1.49	4.76	19.05
	D	65.62	1	13.52	1.57	4.83	14.48
	D	59.99	1	3.08	1.44	4.45	21.04
	D	62.27	2	12.15	1.54	4.41	17.83
	D	60.86	2	15.34	1.52	4.46	17.82
15	D	60.10	3	14.84	1.50	4.71	18.85
	D	57.05	2	15.35	1.54	4.46	17.84
			SrZrO ₃	3.76			
	D	59.15	2	15.38	1.54	4.47	17.89
			SrTiO ₃	1.57			
20	D	58.88	2	15.33	1.53	4.48	17.85
			SrZrO ₃	1.94			
	D	62.25	2	14.04	1.56	4.43	17.73
	D	63.61	2	12.79	1.53	4.41	17.66

25 The capacitor inks can be screen printed onto green
tapes formulated for co-firing onto metal, particularly
kovar, support substrates. The primary crystallizing glass
used is made from a mixture of the following oxides: 29.4%
of ZnO, 24.5% of MgO, 19.6% of B₂O₃, 24.5% of SiO₂ and 2.0%
30 of Co₃O₄, all % by weight. Typical green tape compositions
are given below in Table IV.

TABLE IV

	<u>Additive</u>	<u>Function</u>	<u>Amount, wt%</u> <u>Green tape 1</u>	<u>Amount, wt%</u> <u>Green tape 2</u>
5	Glass	Primary Crystallizing Glass	57.34	57.29
10	Glass P12 ¹	Secondary Crystallizing Glass	6.98	7.03
15	Forsterite ² Powder	Ceramic Filler	7.27	4.42
	Cordierite ³ Powder	Ceramic Filler	1.09	3.44
20	Hypermer PS2 ⁴	Dispersant	0.58	0.58
	Butvar B98 ⁵	Binder	2.04	2.04
25	Santicizer 160 ⁶	Plasticizer	1.36	1.36
	Methyl ethyl Ketone	Solvent	11.67	11.67
30	Anhydrous Ethanol	Solvent	11.67	11.67

¹ Glass composition (wt%) 10.0% Al₂O₃, 42.0% PbO, 38.0% SiO₂, 10.0% ZnO

² 3-5 μ m median particle size

³ 2-3 μ m median particle size

⁴ Registered trademark of ICI Americas, Inc.

⁵ Registered trademark of Monsanto Co.

⁶ Registered trademark of Monsanto Co.

The capacitor inks were screen printed onto the above green tapes in square capacitor patterns 1.27, 2.54 and 5.08 mm in size. Three four-layer green tapes were made with the capacitor ink layer one layer from the top of the stack. The green tapes were laminated at 278 psi and co-laminated to a kovar substrate at 347 psi. A silver-based powder or silver flake-based conductor ink was buried to make a buried co-

fired capacitor. Suitable conductor ink compositions are set forth in Table V.

TABLE V

	<u>Component</u>	<u>Ink 1</u>	<u>Ink 2</u>	<u>Ink 3</u>	<u>Ink 4</u>
5	Silver Powder ¹	83.78			20.11
	Silver-Palladium Powder ¹		84.93		
	Silver Flake ¹			80.97	60.30
10	Glass 3	0.65			
	Dispersant	1.22	1.32	0.53	1.21
	Resin ²	0.88	0.86	0.46	0.46
	Resin ³			1.85	1.84
	Resin ⁴	0.80	0.79		
15	Texanol Solvent	3.22	3.25		
	Terpineol Solvent	6.81	6.73	6.48	6.44
	Butyl Carbitol	2.54	2.12	9.71	9.66

¹ Available from Degussa Corporation, So. Plainfield, NJ

20 ² Ethyl Cellulose Resin N300 of Aqualon Corporation

³ Ethyl cellulose Resin N14

⁴ Elvacite 2045

The resultant laminated stack was fired at 850°C. The capacitance and dielectric loss (tanδ) were measured at 10KHz. The dielectric constant for each capacitor was calculated from the measurement of capacitance (C) in pF, the area (A) of the capacitor in square centimeters and the thickness (t) in centimeters in accordance with the equation

30

$$K = \frac{Ct}{A\epsilon_0}$$

wherein ϵ_0 is a constant = 0.0885pF/cm. These capacitor inks were suitable for operation at high frequency (1GHz). The capacitor sizes and property measurements are given below in Table VI, wherein the thickness is for the fired capacitor, capacitance is measured as pF/mm², dielectric loss is given as tanδ, K is the dielectric constant, and TCC is given in ppm/°C from room temperature (RT) to 125°C. In Table VI, the

40

glass is given in volume % except as otherwise noted.

TABLE VI

	<u>Capacitor Composition</u>	<u>Size, mm</u>	<u>Thick., μm</u>	<u>pF/mm²</u>	<u>Tanδ</u> K	<u>TCC</u>
5	F + 13.4% Glass 1	1.27 5.08	32 32	23.0 18.9	0.010 83 0.011 68	-115 515
10	F + 15% Glass 1	1.27 5.08	32	22.1 10.6	0.007 80 0.012 74.5	582 689
	F + 15% Glass 2	1.27 5.07	30	10.5 9.3	0.007 36 0.008 31.4	878
15	D + 25% Glass 1	1.27 5.08	32	16.1 14.9	0.002 59 0.002 56	
	D + 26% Glass 1	1.27 5.08	32	13.5 10.7	0.003 48.5 0.001 38.4	-1136 37
20	D + 20% Glass 2	1.27	33	30.4	0.007 114	-264
25	D + 25% Glass 2	1.27 5.08	32	15.3 12.7	0.002 55 0.004 46	-560 -342
	D + 30% Glass 3	1.27 5.08	30	13.3 9.8	0.002 45 0.002 33	-918 34
30	D + 25% Glass 2 + 6.6Wt% SrZrO ₃	1.27 5.08	29	40.5 38.6	0.009 131 0.008 125	61 360
35	D + 25% Glass 2 + 2.7Wt% SrZrO ₃	1.27 5.08	34	14.8 10.9	0.003 57 0.003 42	-756 193
40	D + 25% glass 2 + 3.3Wt% SrZrO ₃	1.27 5.08	31	20.7 15.7	0.005 72.3 0.005 55	-119 579

Additional low dielectric constant capacitor inks made of barium titanate were screen printed to form capacitors of various sizes, laminated at 1670 psi, terminated with a silver ink layer, co-laminated to kovar at 1740 psi, and fired at 865°C. Several screen printings were applied to produce a minimum thickness of the fired capacitor. The

composition, size and fired properties are summarized below in Table VII, wherein the glass is given in volume %.

TABLE VII

	<u>Composition</u>	<u>Thick</u> <u>μm</u>	<u>Size</u> <u>mm</u>	<u>pF/mm²</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC</u>
5	25% Glass 2	39	1.27	15.7	71	0.004	-127
			2.54	13.0	56	0.004	201
			5.08	12.6	55	0.004	348
10	25% Glass 2 + 3.3wt% SrZrO ₃	32	1.27	22.7	84	0.007	70
			2.54	20.0	71	0.006	313
			5.08	20.5	74	0.006	453
15	23% Glass 2*	32	1.27	19.7	71	0.003	-118
			2.54	16.2	58	0.003	185
			5.08	15.2	55	0.003	296
20	21% Glass 2	35	1.27	25.0	99	0.004	-69
			2.54	22.4	89	0.004	242
			5.08	22.1	90	0.004	365
	30% Glass 2	35	1.27	14.8	59	0.002	271
			2.54	12.9	51	0.003	360
25			5.08	12.6	50	0.004	411

* IR was measured to be 1.4×10^{12} ohms.

It is apparent that there is a size dependence of capacitance per unit area and dielectric constant for buried capacitors and TCC values. In general, dielectric constant decreases with an increase in capacitor size, as shown in Fig. 1, whereas TCC shows more positive capacitance. The smaller the capacitor, the higher the capacitance, which may be due to fringing capacitance effects and to interaction between capacitors and the surrounding ceramic layers.

Designing high dielectric constant buried co-fired capacitors ($K = 1500$) however, is a much more difficult problem. Since the capacitor dielectric materials have a high sintering temperature, the low firing temperature used

with the present green tapes results in a porous dielectric; the mixture of barium titanate with a low firing temperature glass dilutes the dielectric constant; the surrounding low dielectric constant glass-ceramics diffuse into the capacitor, resulting in further dilution effects; and the diffusion of silver metal into the capacitor also dilutes the dielectric constant. Thus the resultant buried capacitors based on barium titanate were limited to K values of no more than 700, as shown in Tables VIII and IX.

Table VIII summarizes capacitor properties for buried BaTiO₃-based capacitor inks using a silver powder conductor layer. Green tape and capacitor layers were laminated at 280 psi and fired at 850°C. The glass is given in volume %.

TABLE VIII

	<u>Composition</u>	<u>Thick, μm</u>	<u>Size, mm</u>	<u>pF/mm²</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC</u>
15	7.5 vol% Glass 4*	29	1.27 2.54 5.08	123.4 120.22 107.5	404 394 352	0.005 0.007	
20	Same	29	1.27 2.54 5.08	221.3 193.6 187.9	725 634 615	0.008 0.007 0.007	259 313 305
25	The above capacitors were made with a capacitor dielectric ink applied above and below the conductor pads as a barrier						
	7.5 vol% Glass 4**	29	1.27 2.54 5.08	167.4 151.3 154.1	549 496 505	0.008 0.008 0.008	335 423 433
30	7.5 vol% PbTiO ₃ / Bi ₂ O ₃	26	1.27 5.08	150.0 131.2	441 385	0.014 0.013	
35	8.8 vol% Glass 5**	32	1.27 5.08	158.7 160.0	574 586	0.009 0.010	625 550

* using the silver powder as the conductor

** using silver-palladium powder as the conductor

The following capacitors were made, as summarized in Table IX, by laminating green tape and capacitors at 1670 psi and firing at 865°C. The silver conductor used was silver flake. The glass is given as volume %.

TABLE IX

<u>Composition</u>	<u>Thick, μm</u>	<u>Size, mm</u>	<u>pF/mm²</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC</u>
7.5% Glass 4*	27.4	1.27	215.9	668	0.007	104
		2.54	197.9	612	0.007	56
		5.08	214.5	664	0.007	-173
8.8% Glass 5**	27.2	1.27	223.2	686	0.010	166
		2.54	220.2	677	0.010	39
		5.08	222.4	600	0.010	-130
7.5% PbTiO ₃ / Bi ₂ O ₃	25.6	1.27	198.7	575	0.010	
		2.54	186.5	540	0.010	
		5.08	183.6	531	0.009	

* IR was 4.7×10^{10} ohms

** IR was 5.1×10^{10} ohms

The above capacitor compositions were tailored to promote sintering at low temperatures with a minimum dilution of the dielectric constant and to contain less than 10 volume percent of low melting oxides or glass additives made from PbO, B₂O₃, ZnO, CdO or PbTiO₃, materials that are soluble in the BaTiO₃ perovskite lattice structure. These represent fired compositions having a maximum dielectric constant of about 700.

When a low TCC is required, i.e., less than 60 ppm/°C at a temperature range of either between room temperature to -25°C or room temperature to 85°C, a barium titanate-based capacitor formulation also includes a substantial amount of a TCC modifier, SrZrO₃.

Table X illustrates compositions of two such suitable

capacitor inks, given in % by weight.

TABLE X

<u>Composition</u>	<u>Ink 1</u>	<u>Ink 2</u>
BaTiO ₃	47.7	37.5
SrZrO ₃	15.9	30.6
Glass 2	12.4	1.5
Glass 4		6.8
Hypermer PS2	1.5	1.5
Elvacite/solvent	22.5	22.1

A silver-based ink made from 83.78% silver powder, 0.65% glass 3 filler, 4.2% of a mixture of 15% ethylcellulose in a texanol solvent, 7.61% of 13% Elvacite resin in terpeneol solvent, 1.22% of Hypermer PS2 and 2.54% of butyl carbitol solvent. The bottom electrode was screen printed as a single layer, the dielectric layer was screen printed in three layers, and the top electrode singly printed.

The green tape stacks were laminated at 1670 psi and co-laminated to a kovar substrate at 1100 psi and the whole fired at 865°C. The dielectric constant (K) and TCC at two temperatures are given below in Table XI.

TABLE XI

<u>Dielectric</u>	<u>Size, mil</u>	<u>TCC</u>		<u>K</u>
		<u>RT to 85°C</u>	<u>RT to -25°C</u>	
1	200	-47.8	-430.4	77.8
	100	12.0	-441.6	84.5
	50	13.8	-356.7	97.0
2	200	-335.3	-73.5	75.6
	100	-388.2	-28.6	77.6
	50	-440.0	18.3	88.6

A capacitor ink having a low TCC and a low dielectric constant can also be made using titanium oxide (TiO₂) as the dielectric. A dielectric ink was made using 42.1% of TiO₂

powder, 29.6% of glass 2, 1.4% of Hypermer PS2 dispersant and 26.9% of a mixture of 20% of Elvacite resin in terpeneol solvent.

5 The dielectric ink was applied to a green tape at least one layer below the top of the stack, and a termination layer applied thereunder using a conductor ink, and the stack laminated and fired as above. The TCC and dielectric constant K are given in Table XII below.

TABLE XII

10	<u>Size, mm</u>	<u>TCC</u>		<u>K</u>
		<u>RT to 85°C</u>	<u>RT to -25°C</u>	
	1.27	68.6	32.4	25.7
	2.54	14.6	55.4	18.5
15	5.08	3.0	69.8	15.7

In order to achieve higher dielectric constants for buried co-fired capacitors ($K > 1000$), we have found that lead-magnesium-niobate-based (PMN) compositions must be used. Suitable high dielectric constant capacitor ink
20 compositions based on PMN are summarized below in Table XIII, wherein % is by weight.

TABLE XIII

	<u>%PMN</u>	<u>Additives</u>	<u>%</u>	<u>Dispersant</u>	<u>Resin</u>	<u>Solvent</u>
5	75.02	Glass 4 BaTiO ₃	5.33 1.35	1.65	3.33	13.32
	76.88	Glass 4 BaTiO ₃	3.97 1.01	1.61	3.31	13.32
10	74.16	PbTiO ₃ PbO MgO	6.01 1.60 0.20	1.65	3.28	13.11
15	74.93	Glass 5 BaTiO ₂	5.49 1.35	1.65	3.32	13.27
	74.93	Glass 6 PbTiO ₃	5.12 1.72	1.65	3.32	13.27
20	74.70	Glass 5 PbTiO ₃	5.48 1.74	1.64	3.29	13.15

Using the above lead-magnesium-niobate-based capacitor inks and co-firing on alumina support substrates, produced K values of over 2000 with a silver powder conductor ink. However, when buried in green tape laminates on kovar support substrates, the K values were dramatically lowered to about 30-50 due to the dilution effects discussed above. In order to obtain high dielectric constant capacitors on kovar, a barrier layer can be used to block the diffusion of the ceramics into the capacitors during co-firing. This barrier layer can be of a more effective silver metal composition, or of a different dielectric material.

We have found that a BaTiO₃ based capacitor ink can be used as a barrier material when a very low melting glass, lower melting than the glass used in the green tape layers, is used. This barrier glass densifies and crystallizes at a

lower temperature than that required for the green tape glasses to soften significantly. Thus the barrier glass blocks the diffusion of the green tape glasses into the capacitor. In such case the barrier is printed as a pad larger than the capacitor, both below the bottom conductor pad and above the top conductor pad, as shown in Fig. 2. In Fig. 2, a three layer capacitor 12 having a two layer top and bottom conductor layers 14 and 15 respectively is sandwiched between two top and bottom two-layer barrier layers 16 and 17 respectively. The buried capacitor is in turn laminated to top and bottom green tape layers 18 and 19 respectively.

Using a capacitor ink including Glass 6 and 71.07 percent of BaTiO_3 , as described above, a barrier layer was printed as a pad 19x19mm, centered about a capacitor 5.08 x 5.08mm made from a PMN ink including 74.16% of PMN. Silver powder was used to make the conductor ink. Various layers were employed to determine how many barium titanate barrier layers were required to obtain a high dielectric constant capacitor on a kovar supported multilayer circuit board. Controls without the barrier layers were also tested. The test results are given below in Table XIV wherein the number of prints refers to the number of screen prints used for each layer.

TABLE XIV

[illegible]

and the barrier thickness must be about 16-20 microns to be effective.

Further, due to the thickness of the several barrier layers, conductive layers and capacitor layers, the top
5 green tape layer is subject to tearing and care must be taken to prevent that. Further, the large number of screen printing steps required (up to eleven as described above) adds to the costs of the process.

Thus a modified buried conductor ink was sought that
10 would be a more effective barrier, one that would require fewer printing steps and have a reduced thickness that would not subject the top green tape layer to tearing.

We have further found that a mixture of silver flake and silver powder as the conductive layer makes very
15 effective barrier layers, better than using either silver flake or silver powder alone. Silver powder inks produce low dielectric constant capacitors. Silver flake alone formed a very effective barrier layer ($K=3600$) but it resulted in tearing of the overlying green tape layer during lamination
20 or firing. Thus a mixture of 75% by weight of silver flake and 25% by weight of silver powder, although not as effective a barrier as silver flake alone, resulted in high dielectric constant capacitors. However, outgassing of capacitors is a problem during firing. If the silver metal
25 seals the capacitor too well, the gases formed from the additive (PbO containing) materials cannot escape. Thus the silver flake, while it results in a high dielectric constant capacitor, forms a structure that becomes too dense during

firing, and leads to tears in the overlying green tapes.
 Thus the use of a mixture of silver powder and silver flake,
 although a compromise in terms of dielectric constant, does
 not tear the top green tape layer nor do these structures
 have outgassing or bubbling problems.

A plurality of buried PMN-based capacitors on kovar
 substrates were made using silver powder, silver flake and a
 mixed silver powder and silver flake conductor layer. The
 layers were laminated at 1670 psi and fired at 865°C. The
 test results are summarized below in Table XV.

TABLE XV

	<u>Silver</u> <u>Type</u>	<u>#Prints/</u> <u>thick</u>	<u>Thick</u> <u>μm</u>	<u>Size</u> <u>mm</u>	<u>pF/mm²</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC</u>
15	powder	2/10-11 μm	31	1.27 2.54 5.08	14.6 27.7 112.6	51 97 394	0.001 0.010 0.018	-2.0 -6.9
20	powder	2/13μm	35	1.27 2.54 5.08	60.9 230 482.5	246 908 1581	0.009 0.021 0.045	11.4 -16.5 -27.6
25	flake	2/10μm	29	1.27 2.54 5.08	447 716 1066	716 2346 3601	0.027 0.037 0.040	-21.7 -27.6 -30.1
30	flake	1/5μm	21	1.27 2.54 5.08	383 841 1050	928 1967 2498	0.018 0.027 0.026	-30.8 -38.1 -41.9
35	mixed	1/6μm	29	1.27 2.54 5.08	228 477 706	748 1564 2313	0.023 0.033 0.045	-30.8 -39.8 -44.7
40	mixed	2bott/6.5 1 top/3.2 μm	29	1.27 2.54 5.08	624 931 1005	2043 3052 3295	0.025 0.037 0.048	-42.7 -49.1 -51.8

Insulation Resistance (IR) of the first capacitor of
 5.08mm size was 3.8×10^{10} ohms. IR of the second capacitor of
 5.08mm size using silver flake was 6.0×10^{10} ohms. The IR of

the first capacitor using the mixed silver and the same size was 1.0×10^{10} ohms.

The above buried capacitors made with the mixture of silver flake and silver powder as the conductor layer, required fewer printing steps and fired without any problems with bubbling or outgassing. No tearing of the overlying green tape layer was noted.

The dielectric constant of the PMN capacitors exhibit a large size dependence; i.e., the dielectric constant increases with increasing capacitor size, and TCC also increases (becomes more negative) with increasing capacitor size. It is believed this is a result of dilution of the capacitor dielectric by the surrounding low dielectric constant ceramic. Large capacitors have less dilution effect than small capacitors. This is shown in Table XVI below, and schematically in Figs 3 and 4, graphs of dielectric constant and TCC versus capacitor size, respectively. In Table XV the capacitors are based on PMN with mixed silver powder-silver flake inks.

TABLE XVI

	<u>Capacitor</u> <u>Compositn</u>	<u>Fired</u> <u>Thk, μm</u>	<u>Size</u> <u>mm</u>	<u>pF/mm²</u>	<u>K</u>	<u>Tanδ</u>	<u>TCC</u> <u>%</u>	<u>IR</u> <u>$\times 10^{10}$</u>
5	10% glass 4 + BaTiO ₃	22.4	1.27 2.54 5.08	205 496 728	518 1259 1844	0.015 0.018 0.019	-45.5 -55.6 -59.7	1.9
10	7.5% glass 4 + BaTiO ₃	31	1.27 2.54 5.08	7116 334 607	400 1154 2098	0.011 0.017 0.022	-38.4 -50.3 -57.3	
15	10% glass 5 + BaTiO ₃	24	1.27 2.54 5.08	173 508 821	456 1367 2209	0.007 0.008 0.009	-37.6 -47.3 -52.9	1.5
20	10% glass 6 + BaTiO ₃	30	1.27 2.54 5.08	227 253 372	484 870 1279	0.014 0.016 0.018	-24.2 -33.6 -38.4	
25	10% glass 6 + PbTiO ₃	25	1.27 2.54 5.08	68 216 329	196 620 944	0.011 0.016 0.019	-18.1 -24.8 -27.1	

Intermediate range (K=500-700) barium titanate-based buried capacitors fabricated with the same mixed silver flake/powder conductor layers which were also laminated at 1670 psi and fired at 865°C are not as size dependent.

Fig. 5, which is a graph of dielectric constant versus capacitor size using a mixed silver conductor, illustrates the differences in the size dependence of barium titanate-based capacitors and PMN-based capacitors. Thus, for applications requiring intermediate dielectric constant values, barium titanate-based buried capacitors will be more consistent and have lower TCC as compared to PMN-based capacitors.

The buried capacitors of the invention, buried one or two tape layers below the top of the stack, have been

subject to the HHBT reliability test (85°C/85%RH/50VDC) for over 1000 hours with no degradation of the capacitance, dielectric loss or insulation resistance (IR) of the buried capacitors.

5 The above co-fired multilayer ceramic circuit boards having buried capacitors of the invention are useful in various applications, such as cellular telephones.

 The formulation of various resistor inks, method of formation of embedded resistors and test results will be
10 discussed below.

 Resistor inks with resistor values of from 300 ohm/sq to 100 Kohms/sq and a TCR of $<+200$ ppm/°C over a temperature range of room temperature to 125°C, also can be made in accordance with the invention. The target properties for a
5 particular cellular telephone application are 1 Kohm/sq and a TCR less than or equal to 200 ppm/°C over the room temperature to 125°C range.

 The resistor inks are made from a fine particle size, high surface area RuO₂ powder having the characteristics as
10 summarized in Table XVII.

TABLE XVII

<u>Property</u>	<u>Specification</u>
Particle size, microns	0.15 - 0.45
Surface Area (m ² /g)	15 - 25
15 Purity - Wt% Ru	73-76

 The RuO₂ is mixed with one or more glasses to reduce the firing temperature of the conductor powder. Glasses 1 and 3 as set forth above are suitable. A TCR modifier such as BaTiO₃ can also be added.

The above glasses are mixed with the RuO_2 powder, optional modifier and a suitable organic vehicle to form a screen printable composition that can be fired at low temperatures, similar to the firing temperature of the green tape stacks they will be applied to. The resistor ink powder generally contains 17.33 to 24.8% by weight of RuO_2 , 74.3-81.7% by weight of glass 1 and 0.99 to 1.10% by weight of barium titanate. The preferred compositions contain 19.8 to 23.14% by weight of RuO_2 , 75.87 to 79.21% by weight of glass 1 and 0.99 to 1.1% by weight of BaTiO_2 .

Resistor inks were screen printed onto a green tape incorporated into a laminated green tape stack in various patterns (1/2 squares and squares) in sizes from 0.508 x 0.508 to 2.032 x 4.064 mm. Green tape compositions suitable for use herein include the following ingredients, summarized in Table XVIII. The median particle size of the glass and filler materials are given in microns.

TABLE XVIII

	<u>Material</u>	<u>Function</u>	<u>Comp. 1</u>	<u>Comp. 2</u>
5	Glass 2	Crystallizing glass	57.34	57.29
	P12 glass*	Non-crystallizing glass	6.98	7.03
10	Forsterite	Ceramic filler	7.27	4.42
	Cordierite	Ceramic filler	1.09	3.44
15	Hypermer P32 ¹	Dispersant	0.58	0.58
	Butvar B98 ²	Binder	2.04	2.04
	Santicizer 160 ³	Plasticizer	1.36	1.36
20	Methyl ethyl ketone	Solvent	11.67	11.67
	Anhydrous ethanol	Solvent	11.67	11.67

1) Registered Trademark of ICI America Inc

2) Registered Trademark of Monsanto Co.

3) Registered Trademark of Monsanto Co.

The resistors were terminated with a silver conductor ink which was also screen printed. A suitable silver ink composition includes 83.78% by weight of silver powder, 0.65 weight % of glass 3, 1.22 weight% of a dispersant, 0.88 weight % of ethyl cellulose resin, 0.80 of Elvacite 2045 resin (available from Monsanto Company), and a mixed solvent of 3.32 weight % of texanol, 6.81 weight % of terpeneol and 2.54 weight % of butyl carbitol.

The green tape stacks were laminated together and placed on a kovar support substrate and co-fired in air at 850-900°C. The resistors were printed and buried one layer below the top surface of the ceramic stack. After co-firing, the resistors were then connected to the outside by printing

with a silver-palladium or gold conductor ink and post-fired at 700-750°C in air.

Table XIX below summarizes the RuO₂-glass compositions and the properties of the fired resistors. In Table XIX the compositions are given in weight %, and TCR was measured from room temperature to 125°C. A short term overload test (STOL) was also performed.

TABLE XIX

	<u>Composition</u>	<u>R (KΩ/sq)</u>	<u>TCR,</u> <u>ppm/°C</u>	<u>STOL</u>
10	15% RuO ₂ 85% glass 3	99.9	-80	
15	22.5% RuO ₂ 75.5% glass 3 2.0% BaTiO ₃	5.08	-111	200V/5sec/ 0.06% ΔR
20	22.8% RuO ₂ 76.2% glass 3 2.0% BaTiO ₃	4.00	28	
25	24.75% RuO ₂ 74.26% glass 3 0.99% BaTiO ₃	0.86	209	40V/5sec/ 4.5% ΔR
30	21.5% RuO ₂ 77.6% glass 1 0.9% BaTiO ₃	1.01	-20	
	21.6% RuO ₂ 77.9% glass 1 0.5% BaTiO ₃	0.46	153	150V/5sec/ 1.1% ΔR
35	18% RuO ₂ 82% glass 1	0.52	262	
40	10% RuO ₂ 90% glass 1	22.9	44	
	24.8% RuO ₂ 74.3% glass 1 0.99% BaTiO ₃	0.54	25	
45	18.9% RuO ₂ 80.6% glass 1 0.5% BaTiO ₃	0.94	117	

Thus the use of glass 3 was effective to form high value resistors of over 2 Kohms/sq. The glass 1 compositions were chosen for further development of a 1 Kohm/sq resistor.

The above resistor compositions were admixed with an organic vehicle to form an ink composition, using a dispersant (1.44% by weight), ethyl cellulose Resin N300 (0.10% by weight), Elvacite resin 2045 (3.9% by weight) and 25.18% of a mixed solvent of terpineol and butyl carbitol. The resistor ink was adjusted to about 38 volume % solids.

In order to maximize circuit density, it is desirable to print small size resistors such as patterns of 0.508 x 1.016 to 1.016 to 2.032 mm to obtain a 510 ohm resistor. Various resistor inks were made having varying ratios of solids to adjust the resistance and TCR values while keeping the volume % constant at 38%, and maintaining the dispersant concentration constant at 2 weight % of the total powder weight. The powder components of useful resistor inks are summarized below in Table XX.

TABLE XX

20	<u>Material</u>	<u>Composition, Wt%</u>	<u>Preferred composition,</u> <u>Wt%</u>
	RuO ₂	17.33-24.8	19.8-23.14
	Glass 1	74.3-81.7	75.87-79.21
25	BaTiO ₃	0.99-1.10	0.99-1.1

Suitable resistor ink compositions made from the above powder mixtures are shown below in Table XXI.

TABLE XXI

	<u>Material</u>	<u>Function</u>	<u>Ink Compositions, Wt%</u>		
			<u>1</u>	<u>2</u>	<u>3</u>
5	RuO ₂	Conductor	16.70	14.42	14.93
	glass 1	Sintering aid	54.73	57.59	56.15
10	BaTiO ₃	TCR Control	0.71	0.72	
	Hypermer PS2	Dispersant	1.43	1.44	1.45
15	15% Elvacite 2045/terpineol	Binder/solvent	25.12	25.84	25.38
20	7.5% ethyl cellulose N300 in butyl carbi- tol/terpineol	Binder/solvent	1.31	1.32	1.30

After screen printing resistors on one layer of 4-5 layer laminated green tapes as above which had been co-fired onto kovar at 850-900°C, a top surface conductor ink made from silver-palladium or gold was applied and post fired at 750°C. The resistance was measured at DC or low frequency (10KHz) and the TCR was calculated from the resistance measured at room temperature and at 125°C. The results are shown below in Table XXII.

TABLE XXII

	<u>Ink</u>	<u>Size</u> <u>mm</u>	<u>Thick</u> <u>μm</u>	<u>Area</u> <u>(sq)</u>	<u>TCR, co-fired</u>	
					<u>R (KΩ)</u>	<u>ppm/°C</u>
5	2	0.51x1.02	18.3	0.496	0.438	91
		1.02x2.03	18.7	0.496	0.501	10
		1.52x3.05	14.3	0.496	0.563	-18
10	3	0.51x1.02	18.0	0.506	0.434	58
		1.02x2.03	16.0	0.502	0.504	1
		1.52x2.03	14.5	0.505	0.543	-46
15	2	0.51x1.02	19.2	0.461	0.412	62
		1.02x2.03	19.3	0.487	0.503	-59
		1.52c3.05	13.1	0.490	0.617	-64
	<u>Ink</u>	<u>Size</u> <u>mm</u>		<u>R (KΩ)</u>	<u>TCR, post fired</u>	
					<u>ppm°C</u>	<u>R (KΩ/sq)</u>
20	2	0.51x1.02		0.472	85	0.952
		1.02x2.03		0.536	9	1.080
		1.52x3.05		0.598	-34	1.206
25	3	0.51x1.02		0.471	75	0.931
		1.02x2.03		0.542	-9	1.080
		1.52x3.05		0.582	-34	1.154
30	2	0.51x1.02		0.442	58	0.959
		1.02x2.03		0.540	-54	1.109
		1.52x3.05		0.660	-82	1.347

It is apparent that resistance values increase after post firing at 750°C by an average of 7.3%. In addition, resistor values increase with increasing resistor size. This increase in resistance value with increasing size is due to dilution of the resistor by the silver terminating conductor layer during co-firing, which decreases sheet resistance for smaller size resistors.

Additional resistors from resistor ink compositions 1 and 2 are given below in Tables XXIII and XXIV respectively. TCR was measured at room temperature and at 125°C.

TABLE XXIII

	<u>Size,mm</u>	<u>Area,mm²</u>	<u>Resistance (ohms)</u>		<u>Postfired TCR</u>
			<u>Cofired</u>	<u>Postfired</u>	<u>ppm/°C</u>
5	(1) Square Resistors:				
	0.51x0.52	0.258	721	778	-43.4
	1.02x1.02	1.032	922	1003	-94.6
10	1.52x1.52	2.323	976	1064	-111
	(2) 1/2 Resistors:				
	0.51x1.02	0.516	459	496	-55
	1.02x2.03	1.065	498	541	-92
	1.52x3.05	4.645	511	557	-108
15	2.03x4.06	8.258	534	582	-118

The print thickness of the 1/2 sq 1.02x2.03 mm resistor was 18.6 microns.

20

TABLE XXIV

	<u>Size,mm</u>	<u>Area,mm²</u>	<u>Resistance (ohms)</u>		<u>Postfired TCR</u>	<u>Thick</u>
			<u>Co-</u>	<u>Postfired</u>	<u>ppm/°C</u>	<u>(μm)</u>
			<u>fired</u>			
25	(1) Square Resistors:					
	0.51x0.51	0.258	957	1022	-2	
	1.02x1.02	1.032	1086	1172	-55	
	1.52X1.52	2.323	1109	1200	-74	
30	(1/2) Square Resistors:					
	0.51x1.02	0.516	525	563	-9	15.3
	1.02x2.03	2.065	547	591	-53	15.2
35	1.52x3.05	4.645	562	608	-66	13.8
	2.03x4.06	8.258	566	612	-70	

40

The data for resistors of the resistor ink composition 1 is plotted in Figs. 6 and 7 which are graphs of resistance versus resistor area for (1) square resistors and for (1/2) resistors respectively.

The above resistors were also subjected to reliability testing. Test 1 was for 1000 hours at 85°C/85%RH, Test 2 consisted of cycling over 200 times between -55 and 125°C.

Test 3 applied 15.5 Watts/cm² of power to the resistor at 70°C for 1000 hours. The resistors passed these tests.

Resistor ink 1 was used to make a 510 ohm buried resistor 1.016 x 2.032 mm in size in a receiver board
5 designed for operation at 1 GHz. A resistance value of 510 ohms $\pm 10\%$ was obtained after post firing, providing the dried ink thickness was maintained at between 18 and 25 microns.

The ceramic printed circuit boards of the invention are
10 also useful for incorporating or embedding other components, such as RF filters. In such case, thick multilayer stacks that are over 2 mm in thickness after firing are made. However, the large number of green tape layers after firing preclude close control of the shrinkage in the x and y
15 dimensions, and, in addition, the multilayer stack tends to de-laminate from the metal support substrate when fired.

Thus a method had to be developed that would be able to control shrinkage and prevent de-lamination from a metal support substrate over many thicknesses of green tape.
20 We have found that by interleaving green tape layers made from the prior art low dielectric loss glasses mixed with minor amounts of oxide fillers together with green tape layers made from the same glasses but including greater amounts of oxide fillers, many more layers of green tapes
25 can be stacked, laminated and fired with no shrinkage in the x, y directions and no de-lamination from the metal support. These thick multilayer metal supported circuit board stacks are particularly useful when RF components are to be

embedded in the stacks.

Useful prior art glasses used to make one type of green tape are made from zinc-magnesium-borosilicate crystallizing glasses as described above. A suitable
5 crystallizing glass is glass 3 above to which 2.0% by weight of Co_2O_3 coloring agent is added.

This glass is mixed with 9.6% by weight of a non-crystallizing lead-based glass of the lead-zinc-aluminum silicate system. An exemplary glass contains 42.0% by
10 weight of PbO ; 10.0% by weight of Al_2O_3 , 38.8% by weight of SiO_2 and 10.0% by weight of ZnO .

These crystallizing-non-crystallizing glass mixtures are combined with oxide fillers, such as alumina, cordierite, quartz, cristoballite, forsterite and willemite,
15 which serve to control the shrinkage and to further modify the TCE. With the addition of a second oxide filler, the desired dielectric properties, shrinkage characteristics and TCE matched to kovar can all be achieved. For example minor amounts of filler oxides, e.g., 1.5-2% by weight of
20 cordierite and 9.5-10.0% by weight of forsterite, produce excellent ceramics for the present applications.

Thus these glasses have major amounts of glass and minor amounts of oxide fillers (<15%). These glasses have excellent dielectric properties at microwave frequencies,
25 such as 1 GHz. These ceramics are referred to hereinafter as Type I glass-ceramics.

A second type of glass-ceramic is made from the same zinc-magnesium-borosilicate glasses but they include

increased amounts, over about 25% by weight, of oxide fillers. These glasses have lower shrinkage than the Type 1 glass-ceramics, and are referred to hereinafter as Type 2 glass-ceramics.

5 The following Table XXV sets forth examples of different ceramic compositions useful to make the second type of green tape layers.

TABLE XXV

10	<u>Ceramic Composition</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
	Crystallizing glass	50.0	50.0	57.94	66.85
15	Non-crystallizing glass	6.1	6.1	7.04	8.15
	Forsterite	30.0	21.95	30.44	21.70
	Cordierite	13.9	21.95	4.57	3.30
20	Vol. % Glass	50.9	49.1	61.9	72.4
	Vol. % Filler	49.1	50.9	38.1	27.6

25 Thus these ceramics include major amounts of filler, e.g., about 25-50% by weight.

Green tapes are made by formulating the Type 1 and Type 2 glass-ceramics with a resin binder together with plasticizer, dispersants and solvents in known manner, to
 30 form a thick slurry. A typical glass-ceramic composition for use herein has a crystallizing glass particle size of about 10-12.5 microns, a non-crystallizing glass particle size of about 6.5-8 microns, forsterite having a particle size of about 3-5 microns, and cordierite having a particle size of
 35 about 2-3 microns. Table XXVI below sets forth a suitable ceramic green tape formulation in percent by weight.

TABLE XXVI

	<u>Composition</u>	<u>Function</u>	<u>Type 1</u>	<u>Type 2</u>
			<u>Glass/ Ceramic Green Tape</u>	<u>Glass/ Ceramic Green Tape</u>
5	Primary Glass		57.34	31.2-36.4
10	Secondary Glass		6.98	3.8-4.4
	Forsterite powder	Filler	7.27	13.7-16.0
15	Cordierite powder	Filler	1.09	13.7-16.0
	Hypermer® PS2	Dispersant	0.58	0.56-0.79
	Butvar® B98	Binder	2.04	2.13-2.87
20	Santicizer® 160	Plasticizer	1.36	1.42-1.91
	Methyl ethyl ketone	Solvent	11.67	11.58-16.06
25	Anhydrous ethanol	Solvent	11.67	11.58-16.06

The resultant slurry is cast to form a green tape about 0.15-0.20 mm thick, and the green tape is dried.

The two types of green tape using minor and major amounts of amounts of oxide fillers respectively, are then interleaved. Silver or other metal patterns are screen printed on the green tapes to form circuit patterns. Preferably circuit patterns are printed between two green tapes of Type 1, to form a hermetic ceramic, since the Type 2 (high filler content) glass-ceramics tend to become more porous on firing than the Type 1 glass-ceramics.

In order to provide various conductor patterns on the green tapes, a co-firable conductive metal-based thick film conductor ink based on the glass compositions of the invention can be made with a conductive metal powder, such as silver powder, mixed with a small amount of the glasses

disclosed above, together with known dispersants, resins and solvents to form a screen printable conductor ink. Top conductor inks can be made in like fashion using silver-palladium powder, or a gold powder. Via fill inks to connect circuit patterns on various green tape layers together can also be made with silver powder, in known manner.

The green tape stack is then suitably laminated at a pressure of about 1.174 kg/mm² at about 93°C for four minutes, and co-laminated with the prepared metal support substrate at a pressure of about 1.3-1.4kg/mm². After laminating and co-laminating, the multilayer stack on the kovar support is fired in a belt furnace at a belt speed of 0.4 inch/min to a peak temperature of 850-900°C. During firing the organic materials are vaporized, and the low melting glazing glass softens, adhering the multilayer ceramic stack to the metal core. The metal core aids in limiting the shrinkage of the overlying green tapes in the x and y directions. Thus almost all of the shrinkage occurs in the z direction, perpendicular to the metal support. The presence of the interleaved Type 2 glass-ceramics, which have low shrinkage, also serves to constrain the shrinkage of the multilayer stack in the x and y directions.

After firing, a conductive ink may be applied to the top of the fired multilayer stack, as to form bond pads, inductors, microstrip interconnects and the like, in known manner.

The invention will be further described in the following Examples, but the invention is not meant to be

limited to the details described therein. In the Examples, percent is by weight.

Example 1

Eleven layers of Type 1 green tape (A), three of which
5 had a silver-based ink applied thereto (C,D), and 7 layers
of Type 2 green tape (B) were interleaved as shown in Fig.
1. The green tape stack was then laminated and placed over a
kovar support substrate, and co-laminated. The stack was
fired.

10 The shrinkage was 17.0% in the z direction, but only
0.96% in the x direction and 0.61% in the y direction. The
total stack after firing was 2.50 mm thick.

Example 2

Eleven layers of Type I green tape, having metallized
15 planes on three of the layers, were interleaved with Type 2
green tapes, as shown in Fig. 8. Fig. 8 illustrates the Type
1 green tapes as A, Type 2 green tapes as B, C designates
embedded RF filters, and D illustrates silver patterning.
The green tapes were interleaved and stacked, laminated, co-
20 laminated to a kovar support and fired. The fired stack was
2.40 mm thick.

The shrinkage was 17.0% in the z direction, 0.64% in
the x direction and 0.60% in the y direction.

Example 3

25 Eleven layers of Type 1 green tape and 7 layers of
Type 2 green tape were interleaved and stacked, laminated
and fired. The resultant stack was 2.20 mm thick.

The shrinkage was about 17% in the z direction, 0.83%

in the x direction and 0.98% in the y direction.

Example 4

5 Fifteen layers of Type 1 (A) green tape having
embedded filters (C) on one layer and ground planes (D) on
two layers, as shown in Fig. 9, and 8 layers of Type 2 green
tape (B) were interleaved and stacked, laminated and fired
to form a stack 2.52 mm in thickness.

The shrinkage was about 17% in the z direction, 0.35%
in the x direction and 0.85% in the y direction.

10 The physical properties of the resultant multilayer
tapes alone. The results are given below in Table XXVII.

TABLE XXVII

5	<u>Property</u>	<u>Type I tape alone*</u>	<u>Interleaved with Type 2 tape **</u>
	TCE (25-300°C)	6.3 ppm/°C * 7.7 ppm/°C **	
	Dielectric Constant	6.8 @ 1GHz	5.4 @ 12 GHz
10	Dielectric Loss (tanδ)	0.001 @ 1GHz	0.0018 @ 12 GHz
	Volume Resistivity, (II-cm)	1.5 x 10 ¹⁴	
	Surface Resistivity, (II-cm)	>1.0 x 10 ¹²	
15	Chemical Durability	pass	
	Buried Conductor		
	Resistance	3.6mΩ/square	
	Via conductor		
	Resistance	0.72 mΩ/via	
20	* on kovar		
	** ceramic alone		

Example 5

Properties of various Type I and Type 2 green tape
stacks were fired at 865°C and their properties measured. The
results are summarized below in Table XXVIII

TABLE XXVIII

30	<u>Sample Stack</u>	<u>Fired Density</u>	<u>ε</u>	<u>Tanδ</u>	<u>Frequency</u>
	5 layers Type 1	3.14 g/cc	6.41	0.0023	15.6 GHz
	5 layers Type 2	2.01 g/cc	3.64	0.0017	17.9 GHz
	23 layers, of Example 4		5.39	0.0018	11.6 GHz
35	20 interleaved layers		5.24	0.0019	12.2 GHz

Thus the interleaved green tape layers can be stacked
to produce thick fired metal supported multilayer circuit
boards that shrink in only one dimension.

Although the invention has been described in terms of
specific embodiments, it will be clear to those skilled in

the art that variations in the glass compositions, the amounts of oxide fillers, the metal support, the number of green tape layers, the types of capacitors and capacitor inks, resistors and resistor inks and conductors and
5 conductor inks and the like can be made and are meant to be included herein. The invention is only to be limited by the appended claims.

We Claim:

1. A supported ceramic circuit board having an embedded component therein comprising

- a) a laminated green tape stack on a kovar support;
- 5 b) a screen printed component screen printed onto a green tape layer from an ink comprising a dielectric and a low melt temperature glass,
- c) a conductor layer below said screen printed component and
- 10 d) an overlying green tape layer.

2. A supported ceramic circuit board having embedded components comprising:

- a) a laminated green tape stack on a kovar support;
- b) a buried screen printed capacitor made from a
- 15 dielectric selected from the group consisting of barium titanate, titanium oxide and lead-magnesium-niobate;
- c) a silver conductor layer printed below and above the capacitor; and
- d) an overlying green tape layer.

20 3. A supported ceramic circuit board according to claim 2 wherein said capacitor is sandwiched between silver barrier layers, said barrier layer comprised of a mixture of silver powder and silver flake.

25 4. A supported ceramic circuit board according to claim 2 wherein said dielectric is lead-magnesium-niobate, and said capacitor is sandwiched between silver or barium titanate barrier layers, said capacitors having a high dielectric constant over 700.

5. A green tape stack which, when fired, is at least two millimeters thick comprising

alternating green tape layers of a first type comprising
5 a mixture of crystallizing and non-crystallizing glasses
together with at least 5% up to 15% by weight of an oxide
filler, with green tape layers of a second type comprising a
mixture of crystallizing and non-crystallizing glasses
together with a higher percent by weight of an oxide filler
10 than the first type, onto a metal support substrate.

6. A green tape stack according to claim 5 wherein said non-crystallizing glass is made from PbO , Al_2O_3 , and SiO_2 .

7. A green tape stack according to claim 5 wherein said
oxide filler is selected from the group consisting of
15 alumina, cordierite, quartz, cristobalite, forsterite and
willemite.

8. A green tape stack according to claim 5 wherein said
metal support substrate is a copper-nickel clad or plated
kovar support.

20 9. A green tape stack according to claim 5 wherein a
conductive layer is screen printed between one or more green
tape layers of the first type.

10. A green tape stack according to claim 9 wherein said
conductive layer is a silver-based layer.

25 11. A green tape stack according to claim 9 wherein a
conductive layer is screen printed onto the top surface of
the stack.

12. A fired green tape stack according to claim 5.

45

13. A fired green tape according to claim 5 wherein an RF component is embedded in the green tape stack.

14. A multilayer ceramic green tape structure comprising a plurality of low firing temperature green tapes that do not shrink in the x and y dimensions during firing having
5 circuit patterns thereon mounted on a metal support substrate, a capacitor screen printed on a green tape layer one or more layers below the top of the stack, and a conductor layer screen printed above and below the
10 capacitor.

15. A multilayer ceramic green tape structure according to claim 14 wherein said capacitor layer is made from barium titanate, titanium oxide or lead-magnesium-niobate.

16. A multilayer ceramic green tape structure according to
15 claim 14 wherein the conductor layer is of silver.

17. A multilayer ceramic green tape structure according to claim 14 wherein said capacitor is sandwiched between two barium titanate barrier layers having a thickness sufficient to prevent diffusion of the green tape glasses into the
20 capacitor during firing.

18. A method of forming embedded components in a multilayer ceramic circuit board on a metal support substrate comprising

- 5 a) forming a component precursor ink of a precursor compound, a low firing temperature glass and an organic vehicle;
- b) screen printing a bottom conductor layer;
- c) screen printing the component precursor ink over the bottom conductor layer;
- 10 d) covering said screened component precursor ink layer with one or two layers of green tape;
- e) screen printing a top conductor layer;
- f) aligning and laminating said layers together, and
- g) firing said laminated layers.

19. A method of forming embedded capacitors in a multilayer ceramic circuit board on a metal support substrate comprising

- 5 a) forming a capacitor ink from a mixture of a dielectric selected from the group consisting of barium titanate, titanium oxide and lead-magnesium-niobate, a low firing temperature glass and an organic vehicle;
- b) screen printing a bottom conductor layer;
- 10 c) screen printing capacitors over the bottom conductor layer;
- d) screen printing a top conductor layer;
- e) covering said capacitors with one or more layers of green tape;
- 15 f) aligning and laminating said layers together, and
- g) firing said laminated layers.

20. A capacitor ink comprising a dielectric selected from the group consisting of barium titanate, titanium oxide and lead-magnesium niobate, a low firing temperature glass and
20 an organic vehicle.

21. A resistor ink composition comprising ruthenium oxide, a low firing temperature glass in sufficient amount to reduce the firing temperature of the mixture within the range 850-900°C and an organic vehicle.

22. A resistor ink composition according to claim 20 further including a TCR modifier of barium titanate.

23. A ceramic multilayer printed circuit board including
5 embedded resistors comprising a screen printed resistor layer of ruthenium oxide and a low firing temperature glass covered with one or two layers of green tape, said layer printed onto a green tape stack laminated to a metal support board and a conductor layer underlying said resistor layer.

10 24. A ceramic multilayer printed circuit board according to claim 22 wherein said metal support board is of kovar.

25. A method of making embedded resistors comprising

a) forming a resistor ink comprising ruthenium oxide
mixed with a sufficient amount of a low firing temperature
15 glass so that the mixture has a firing temperature between about 850-900°C together with an organic vehicle;

b) screen printing the ink on a green tape stack to deposit resistors thereon;

c) covering said resistor layer with one or two green
20 tape layers; and

d) terminating the resistors with an underlying first conductive layer,

e) laminating the resultant green tape stack;

f) firing said stack to a temperature of from about
25 850-900°C,

g) coating the top surface of the fired stack with a second conductive layer, and

h) post firing said fired multilayers.

FIG. 1

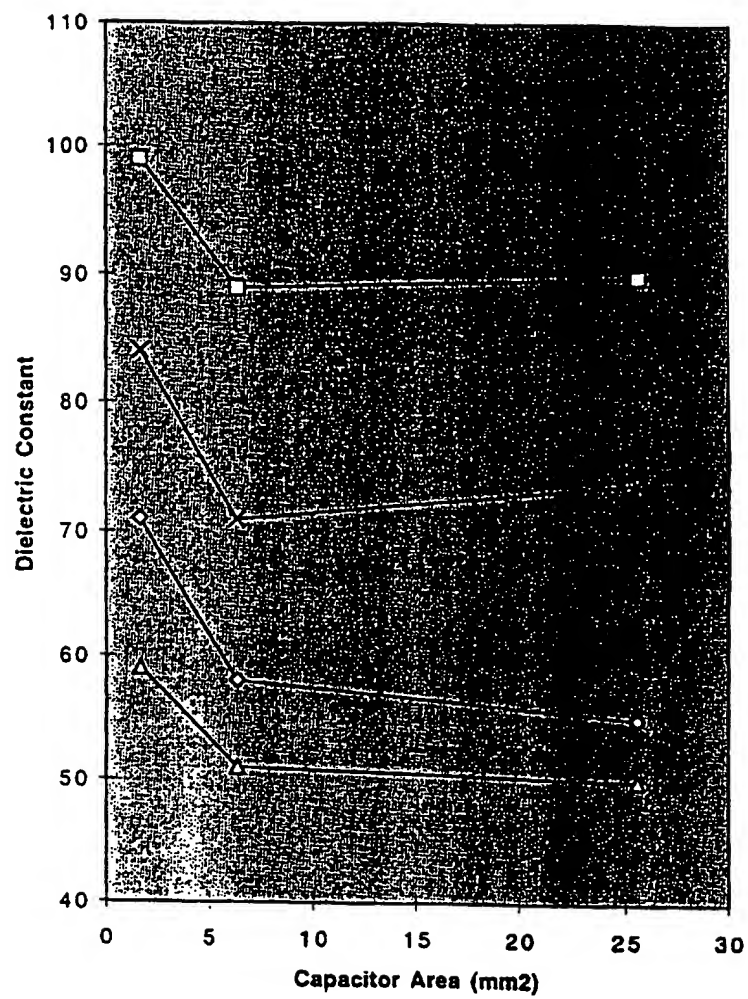


Fig. 2

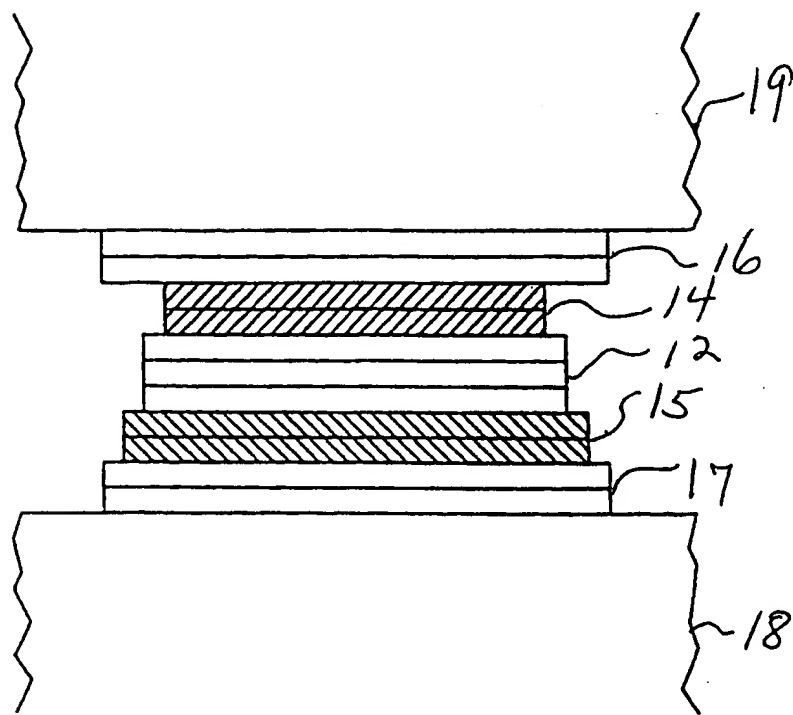


FIG. 3

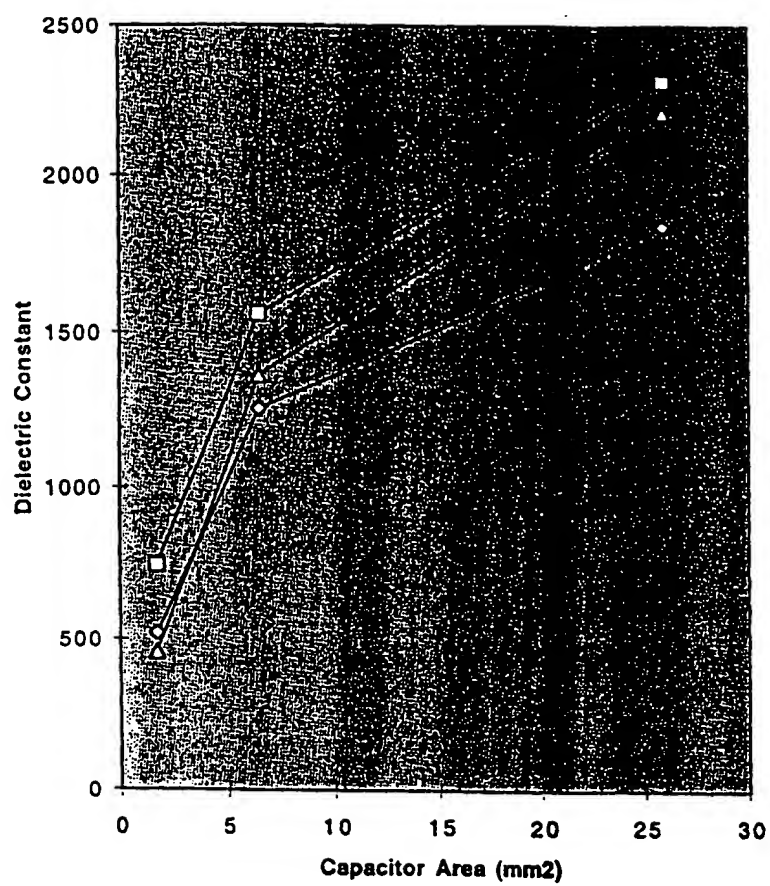


FIG-4.

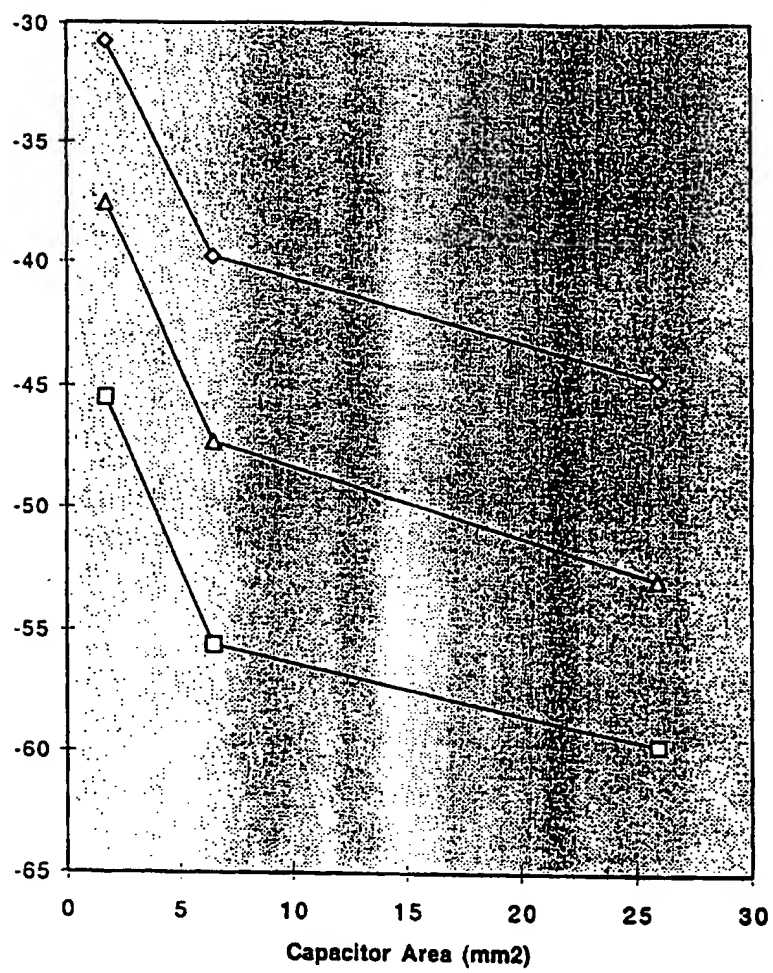


FIG-5

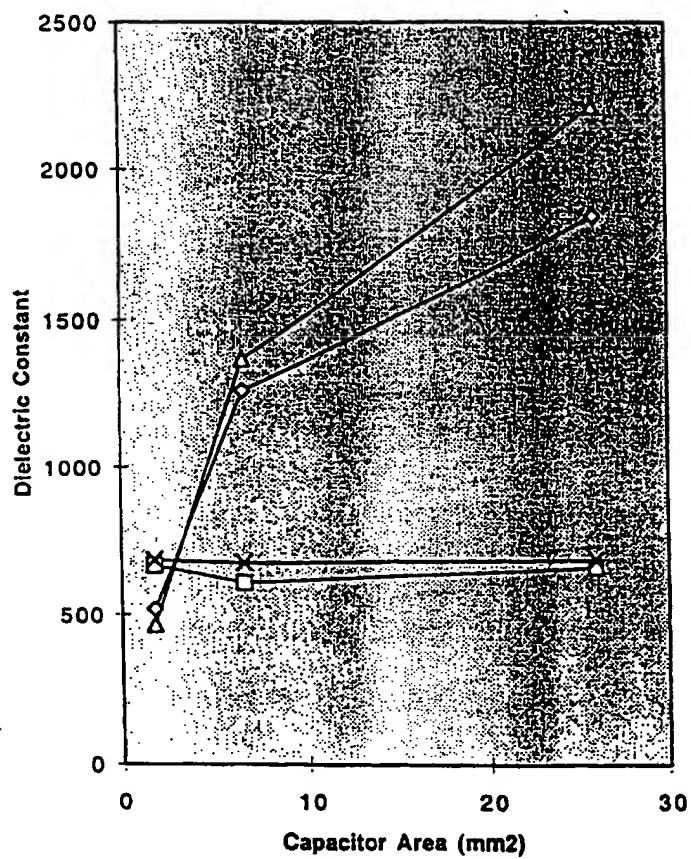


FIG-6

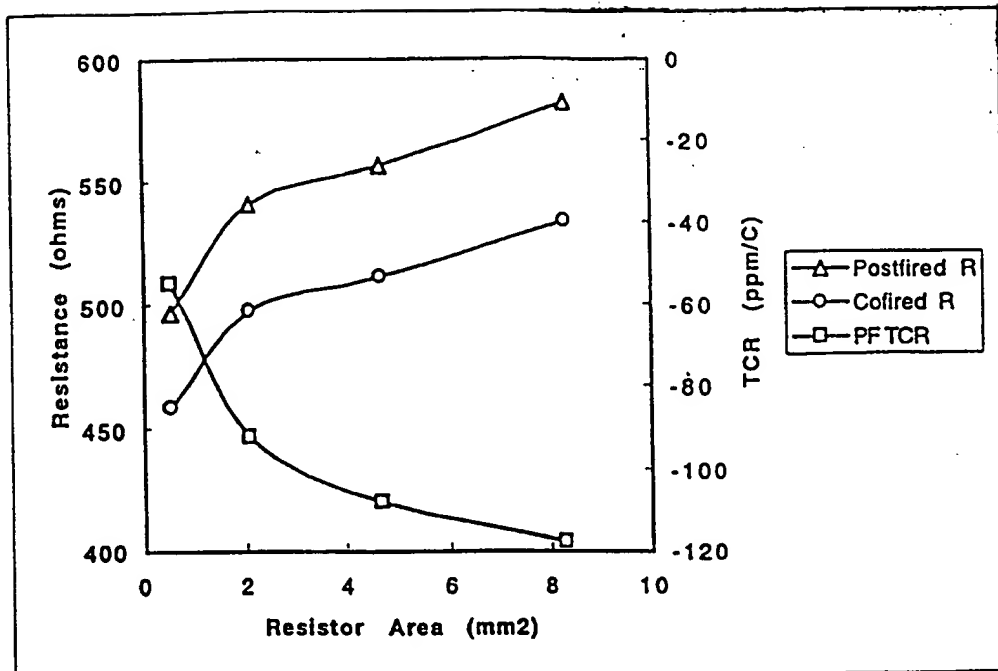


FIG-7

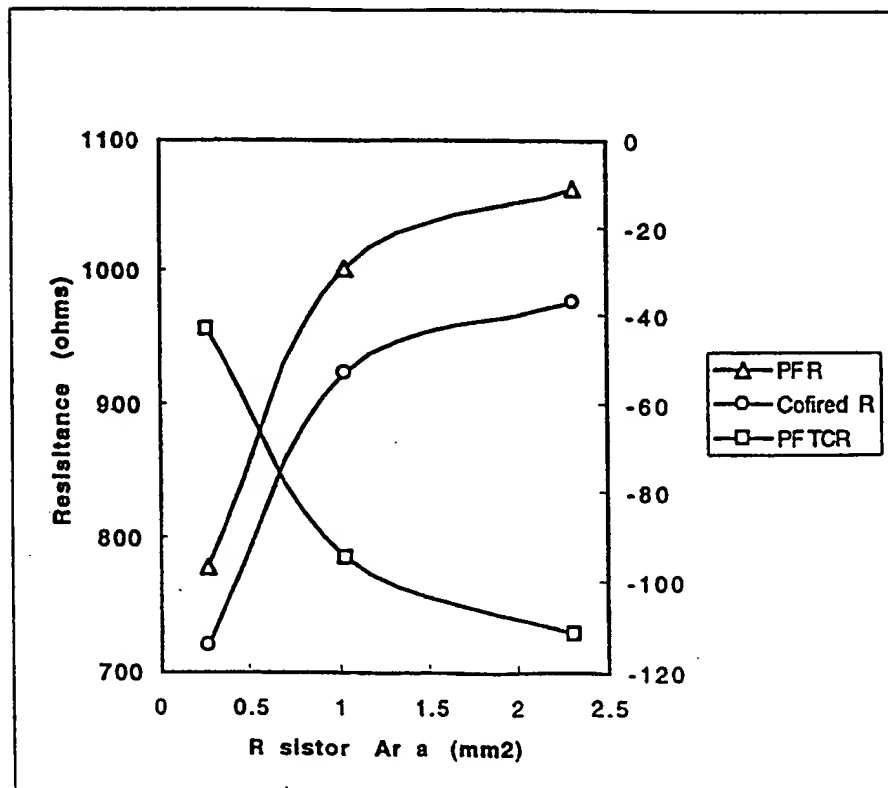


FIG. 8

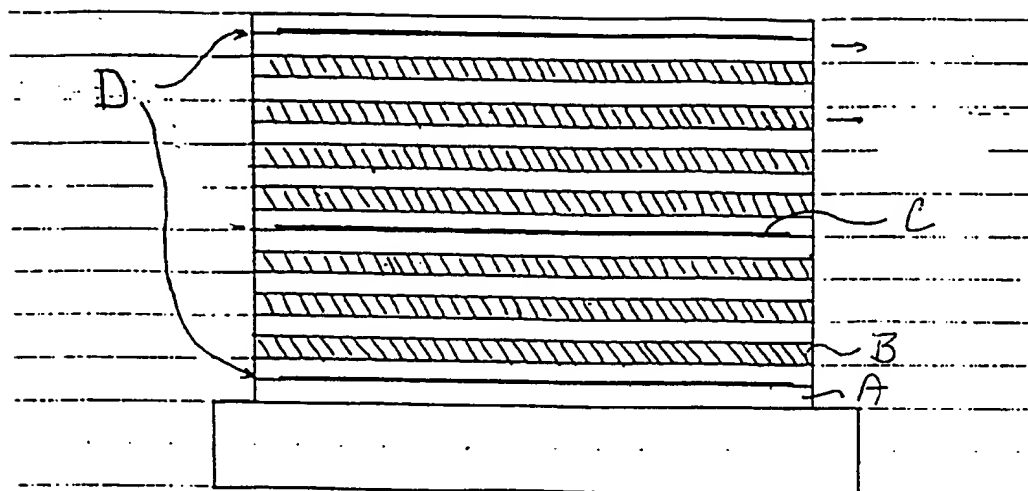
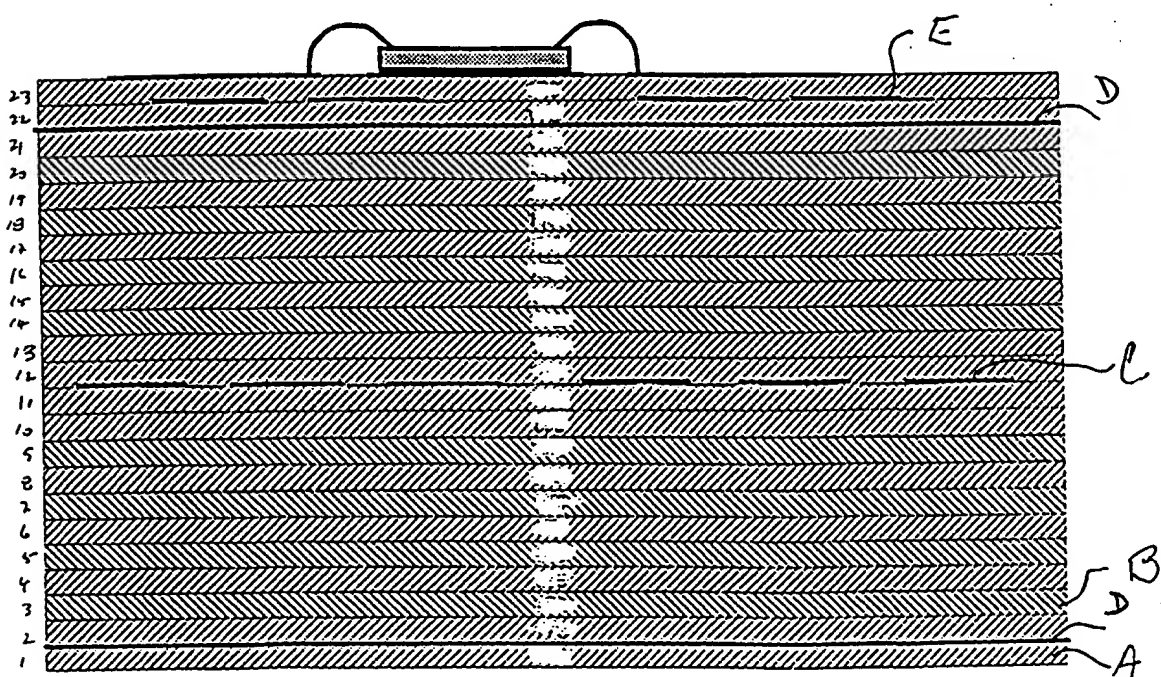


FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/03270

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,708,570 A (POLINSKI, SR) 13 January 1998 (13/01/98), see entire document.	1-3, 14
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Y		20
--		-----
A	US 5,581,876 A (PRABHU et al.) 10 December 1996 (10/12/96), see entire document.	4-13, 15-19
Y		20
A		1-20
A		21, 23, 25
A	US 5,256,469 A (CHERUKURI et al.) 26 October 1993 (26/10/93), see entire document.	1-20
A	US 5,166,658 A (FANG et al.) 24 November 1992 (24/11/92), see entire document.	21, 23, 25
A	US 5,657,199 A (DEVOE et al.) 12 August 1997 (12/08/97), see entire document.	1-20

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

11 MAY 1998

Date of mailing of the international search report

07 JUL 1998

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
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 Telephone No. (703) 308-0640

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03270

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,148,005 A (FANG et al.) 15 September 1992 (15/09/92), see entire document.	1-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03270

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 22, 24
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Please See Extra Sheet.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03270

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

H01G 4/06, 4/20, 4/228, 4/10; H01C 10/10, 10/00, 7/10; H01L 27/108 23/02

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

361/313, 301.4, 306.3, 311, 312, 320, 321.1, 321.2, 321.3, 321.4, 321.5, 322, 762; 257/532, 306, 303, 310, 302, 307, 686; 438/253, 109, 438, 269, 253, 250, 455, 243, 245, 239; 338/23, 309, 195, 49; 219/505; 427/102,103, 101; 252/514, 62.3R, 62.9PZ, 62.3Q; 501/134, 136, 137, 138

B. FIELDS SEARCHED

Minimum documentation searched
Classification System: U.S.

361/313, 301.4, 306.3, 311, 312, 320, 321.1, 321.2, 321.3, 321.4, 321.5, 322, 762; 257/532, 306, 303, 310, 302, 307, 686; 438/253, 109, 438, 269, 253, 250, 455, 243, 245, 239; 338/23, 309, 195, 49; 219/505; 427/102,103, 101; 252/514, 62.3R, 62.9PZ, 62.3Q; 501/134, 136, 137, 138

BOX I. OBSERVATIONS WHERE CLAIMS WERE FOUND UNSEARCHABLE

2. Where no meaningful search could be carried out, specifically:

Claim 22 recites "A resistor ink compositon" which depends from claim 20 which recites "a capacitor ink" therefore the examiner can not search claim 22 due to claim 22 depends on previous claim 20 which has unrelated subject matter.

Claim 24 recites "A ceramic multilayer printed circuit board" depends from claim 22 which recites "A resistor ink", therefore the examiner can not search claim 24 due to tclaim 24 depends from previous clam 22 which has unrelated subject matter.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-4, drawn to a supported ceramic cirucit board.

Group II, claim(s) 5-13, drawn to a green tape stack.

Group III, claim(s) 14-17, drawn to multilayer ceramic green tape.

Group IV, claim(s) 18, drawn to a method of forming embedded component.

Group V, claim(s) 19, drawn to a method of forming embedded capacitors in a multilayer ceramic circuit board.

Group VI, claim(s) 20, 22, and 24, drawn to a capacitor ink.

Group VII, claim(s) 21, drawn to a resistor ink.

Group VIII, claim(s) 23, drawn to a ceramic multilayer printed circuit board included embedded resistors.

Group IX, claim(s) 25, drawn to a method for making embedded resistors.

The inventions listed as Groups I-IX do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The invention of Group I purports a supported ceramic cirucit board while Group II purports a green tape stack while Group III purports a multilayer ceramic green tape while Group IV purports a method of forming embedded component while Group V purports a method of forming embedded component while Group VI purports a capacitor ink while claim VII a resistor ink while Group VIII purports a ceramic multilayer printed circuit board included embedded resistors while